Determination of Equilibrium Constant of an Indicator

PURPOSE

- Calculate the molar extinction coefficient ε of the protonated and unprotonated forms of bromocresol green
- Determine experimentally the equilibrium constant (K_{In}) for bromocresol green, and compare the result with the theoretical K_{In} value

INTRODUCTION

An **indicator** is used to highlight the endpoint of a titration by changing color near the pH at which the stoichiometic endpoint of the reaction between acid and base is reached. For example:

$$\underset{\text{Yellow}}{HIn_{(aq)}} \leftrightarrow H^+_{(aq)} + \underset{\text{Blue}}{In^-_{(aq)}} \qquad K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

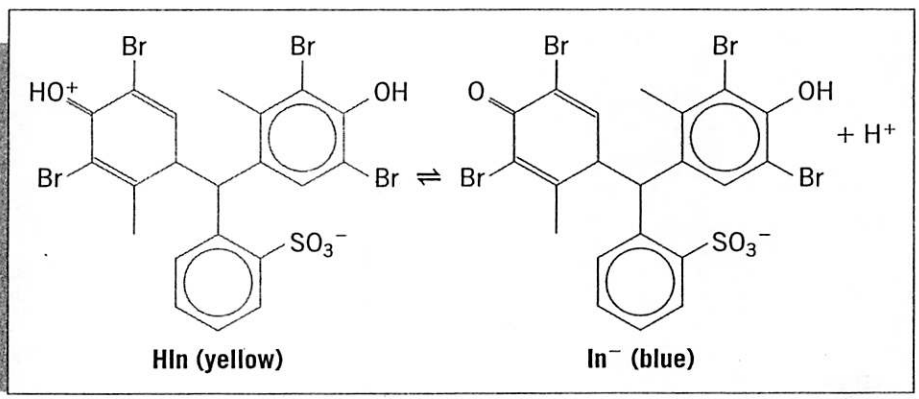

Figure 11.1 The protonated form of bromocresol green (HIn) is yellow. The loss of the proton results in the conjugate base form (In^-), which is blue.

Because indicators are weak acids themselves, they have acid and conjugate base pairs. The ratio of concentrations of these species at a given pH can be used to calculate the K_a of the indicator. Indicators have different chemical structures in the protonated and unprotonated form. It is the loss of the proton that is responsible for the color change. The protonated form has its own unique absorbance spectrum, as does the unprotonated form. As with any equilibrium system, all species must be present at equilibrium. When the absorbance of a sample of indicator is measured, this is the sum of the absorbances—from both the protonated and unprotonated forms—at the wavelength chosen. An aqueous solution of bromocresol green is green at pH 5.0 because it contains a mixture of both the protonated form, which is yellow, and the unprotonated form, which is blue. This experiment is designed so that you can decipher the amount of light absorbed by a sample of known pH at a given wavelength by each form of the indicator.

The absorbance of light at a given wavelength is directly proportional to concentration if the pathlength of the cuvette is constant. The absorbance is described by **Beer's Law**:

$$A = \varepsilon Cl$$

where A is absorbance at a given wavelength; C is concentration in moles per liter; l is pathlength of cuvette in cm; and ε is the molar extinction coefficient in $M^{-1}cm^{-1}$, which is unique at each wavelength for each compound (a larger ε indicates that the compound absorbs more energy at this given wavelength).

Beer's Law is sometimes written as $A = abc$, where A is absorbance at a given wavelength, a the molar extinction coefficient, b the cuvette pathlength in cm, and c the solution concentration in molarity. *However, note:* this linear relationship is correct only when the absorbance is 2 or less.

Procedure Preview If bromocresol green is used as an indicator in an acid-strong base titration, a color change from yellow to blue will show the endpoint of the titration. To quantify the amount of the measured absorbance due to the protonated form of the indicator, a large excess of the strong acid HCl is added. Under these conditions, it is reasonable to assume that all of the indicator is protonated, thus allowing the absorbance of the light at this wavelength to be assigned to a known concentration of protonated indicator, HIn. Now the equation

$$\frac{A}{C} = \varepsilon l$$

can be used to calculate concentration. The pathlength, l, of the cuvettes used must be constant, but this is easy to ensure by treating another sample with a large excess of NaOH, so that

$$\frac{A}{C} = \varepsilon l$$

can also be calculated for In^-, the unprotonated form of the indicator. A buffer of known pH (therefore known $[H^+]$) is mixed with the indicator and, using the calculated extinction coefficients, $[H^+]$ is used to calculate K_{In}. Finally, the pH of a buffer solution will be determined.

Pre-Lab Questions

1. What is an indicator? How does an indicator work?
2. Look in your textbook, or a reference book like the *CRC* or the *Merck Index*, to find the theoretical K_{In} of bromocresol green.
3. What is a buffer?
4. Calculate the volume of 0.100 *M* sodium acetate that must be mixed with 20.00 mL of 0.100 *M* acetic acid to make a buffer of pH 4.30, assuming volumes are additive.
5. Can bromocresol green be accurately used to show the endpoint of titration
   a. between the strong base NaOH and the strong acid HCl? Explain.
   b. between the strong base NaOH and the weak acid CH_3COOH? Explain.

MATERIALS

- device to measure 4.50 mL of solution (50-mL buret, 10-mL variable volume pipet, or 10-mL graduated cylinder)
- spectrophotometer (Spectronic 20 or colorimeter)
- cuvettes/test tubes (all of same or known pathlength; your instructor will explain how to test for consistent pathlength)
- ~5×10^{-5} *M* bromocresol green solution
- 0.10 *M* HCl
- 0.10 *M* NaOH
- distilled water
- pH meter
- standard pH buffers (of 4.00 and 10.00)
- 0.100 *M* acetic acid solution
- 0.100 *M* sodium acetate solution
- buffer of unknown pH
- parafilm
- stirring rod

PROCEDURE

I. Making Indicator and Buffer Solutions

Step A Place 4.50 mL of the bromocresol green solution in each of 6 test tubes.

Step B Add 4.50 mL of 0.100 *M* HCl to 2 test tubes already containing the indicator.

Step C Add 4.50 mL of 0.100 *M* NaOH to 2 test tubes already containing the indicator.

Step D Mix the solutions thoroughly by using a new transfer pipet for each sample (or tightly cover each test tube with a piece of parafilm and invert a few times).

Step E Make the buffer by mixing the appropriate volumes of 0.100 *M* acetic acid and 0.100 *M* sodium acetate, which you calculated in Pre-Lab Question 4.

Step F Calibrate the pH probe as directed by your teacher.

Step G Measure the pH of your buffer, taking time to let the reading become steady.

Step H Add 4.50 mL of your buffer to 2 test tubes, each containing 4.50 mL of bromocresol green indicator.

Step I Add 4.50 mL of the buffer of unknown pH to 2 test tubes, each containing 4.50 mL of bromocresol green indicator.

II. Measuring Absorbance

Step A Be sure that the spectrophotometer has warmed up for at least 20 minutes at 615 nm before continuing to Step B. If you are using a colorimeter, you need to assemble it before going to Step B.

Step B Calibrate the spectrophotometer or colorimeter as directed by your instructor. Be sure to use distilled water as a blank.

Step C Fill a cuvette with each sample.

Step D Dip the cuvette in mild detergent solution, rinse and blot dry. Be sure the cuvette is clear of particulates or gas bubbles.

Step E Place the cuvette in the spectrophotometer (or colorimeter). Allow the absorbance reading to become constant before recording it.

Step F Repeat Step E for all samples.

Calculations

1. Present all your experimental data in tabular form.
2. Calculate the molar extinction coefficient (ε) of HIn, the protonated form of bromocresol green. Use the absorbance of the sample with excess acid, if you know the pathlength of the cuvette, or $\varepsilon_{HIn}l$ of these, if you do not know the pathlength.
3. Calculate the molar extinction coefficient (ε) of In^-, the unprotonated form of bromocresol green. Use the absorbance of the sample with excess base, if you know the pathlength of the cuvette, or $\varepsilon_{In^-}l$ of these, if you do not.
4. Set up two equations containing [HIn] and $[In^-]$ and solve for each. You will need to use
   a. $A = \varepsilon_{HIn}l\,[HIn] + \varepsilon_{In^-}l[In^-]$ *and*
   b. your two calculated extinction coefficients; the absorbance of the buffer sample you made; and the fact that $[HIn]_0 = [In^-]_{eq} + [HIn]_{eq}$.
5. Calculate K_{In} for bromocresol green for each of the buffer solution/indicator mixtures.
6. Determine the pH of the unknown buffer. Use the relationships outlined in calculation 4; your K_{In} for bromocresol green; and the absorbance of the solution of bromocresol green and buffer of unknown pH in your calculations.
7. Compare your experimental constant for bromocresol green with the theoretical value.
8. Using your answer to calculation 5, propose and explain two possible sources of experimental error that would explain your actual results.

Post-Lab Questions

1. Why did the buffer used in this experiment to help determine the K_{In} have a pH of 4.30, and not of 9.00? Explain your answer in detail.
2. Would the pH of the buffer you made be more acidic, more basic, or the same if you had mistakenly added an additional 2.00 mL of sodium acetate solution? Thoroughly explain.
3. Would this experimental procedure need to be modified to find the K_{In} of phenolphthalein? Explain any changes that would need to be made in detail.
4. Could this experimental procedure be used to successfully determine the K_{In} of the **Universal Indicator**? Explain why or why not.